DISPLACEMENTS OF HYDROXYL FREQUENCIES IN SOLUTION AND SOLID STATE

BY

IVAR TRYGVE KROHN

Bach. of Chem., University of Minnesota, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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ACKNOWLEDGMENT

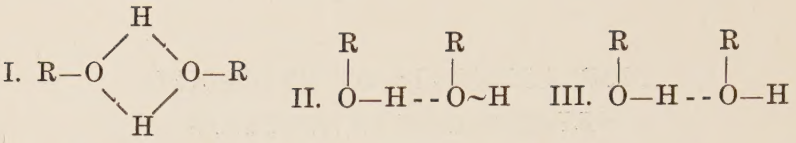
The author wishes to express his sincere appreciation to Professor W. H. Rodebush for initiating and directing this research; also to Professor A. M. Buswell, Dr. F. T. Wall and Dr. R. C. Gore for their many helpful suggestions.

DISPLACEMENTS OF HYDROXYL FREQUENCIES IN SOLUTION AND SOLID STATE

Introduction. The use of infrared in chemistry has assumed a position of great importance within the last few years. It has provided a sensitive tool in supplementing other methods of research and in determining some of the finer structures of the molecule. In the present investigation the infrared technique has been used for the detection of hydrogen bonding between molecules in solution and in the solid state.

The purpose of this investigation is to determine the displacements of the fundamental hydroxyl vibrational frequencies of various compounds in an inert solvent (carbon tetrachloride), in carbon tetrachloride in the presence of a donor molecule (diethyl ether), and in the solid state. The spectra of several phenols are determined in carbon tetrachloride solution in an attempt to arrive at some conclusions concerning the manner in which these phenols associate and to correlate the observed displacements of the hydroxyl frequencies with this model. For this purpose several different concentrations are used for each compound. In addition the effect of an adjacent halogen atom or hydroxyl group is determined. The displacements of the hydroxyl frequencies when association occurs with a different molecule, diethyl ether, are classified and discussed in relation to several physical properties of the hydroxyl compounds. Finally, the spectra of the compounds in the solid state are found. It is hoped that some evidence may be obtained which will establish the cause of the large shift in the position of the association band when the liquid becomes a solid.

There are several ways in which the phenols may be postulated to associate among themselves through the hydroxyl group in the dimer stage. These are



Models II and III differ with respect to the unbonded hydroxyl group. In model II the frequency of the unbonded hydroxyl group is assumed to be effected by the hydrogen bonding whereas in model III this is not the case.

The alcohols have been found to associate in accordance with model I; however in the case of the phenols there is still some doubt as to the method of association. Fox and Martin[1] have found evidence for the existence of dimers of type II in the case of benzyl alcohol; and although they present no evidence for this type of association for phenol besides the fact that their equilibrium calculations favor dimers I and II, they believe that model II represents the actual case. From the low value of the bonding energy for the dimers of phenol Lassettre[2] concludes that the dimer of type II or III is the only one possible.

A great deal of work has been done with regard to the association between unlike molecules. Gordy[3] has investigated the displacement of the OD frequency in the presence of many different solvents. He found that the displacement of the OD frequency was approximately proportional to the basicity of the donor atom and that the displacement had no apparent relation to the dipole moment of the solvent or to the strength of the bond.

Brattain[4] found that phenol showed a very interesting shift in the position of the association band, 2.96 μ to 3.10 μ, in passing from the liquid state to the solid state. Water also gave a similar shift. Brattain postulated that the source of this large shift is either an increase in association in the solid state or the effect of lattice forces. Davies[5] has determined the solid absorption spectra of several types of organic compounds. His results are, in general, complex and difficult to interpret.

Results and discussion. Table I contains the data obtained for the phenols in carbon tetrachloride solution.

Table I

Compound	Fund.		Dimer		Trimer		Cono.
	μ	cm.$^{-1}$	μ	cm.$^{-1}$	μ	cm.$^{-1}$	M.
Phenol	2.76	3623	2.86	3497	2.95	3390	0.352
p-Bromophenol	2.76	3623	2.86	3497	.....	.....	0.294
p-Chlorophenol	2.76	3623	2.86	3497	.....	.....	0.2089
o-Cresol	2.76	3623	2.85	3509	.....	.....	0.488
m-Cresol	2.76	3623	2.85	3509	2.95	3390	0.416
p-Cresol	2.76	3623	2.85	3509	2.95	3390	0.436
p-Nitrophenol	2.76	3623	2.91	3436	.....	.....	Satd.

The terms "Fund.", "Dimer", and "Trimer" refer to the fundamental monomer band, and the associated dimer and tramer bands, respectively. The values in the last column refer to the highest concentrations of the phenol used.

The dimer equilibrium constant for the association of the phenols was calculated by means of three equations.

$$1.\quad K=\frac{1-\alpha}{2\alpha^2 C}\cdot \qquad 2.\quad K=\frac{1-\alpha}{C(2\alpha-1)^2}$$

$$3.\quad K=\frac{\alpha C}{1-\alpha^{\frac{1}{2}}}$$

where C=the molar concentration of the phenol.

α=the fraction of free hydroxyl groups present.

The first equation is based upon the postulated model I & II (page 2) of the dimer in which neither hydroxyl group contributes to the monomer band of the spectrum; the second model III (page 2) in which one group contributes to the monomer band while the other gives rise to the dimer band; the third is an equation given by Mecke[6]. The results of the calculations are shown in Table II.

Table II

Substance	Conc.	α	K_1	K_2	K_3
Phenol	0.022	0.94	1.47	3.3	0.74
	0.044	0.89	1.57	4.1	0.63
	0.088	0.81	1.71	6.0	0.69
p-Bromophenol	0.0735	0.88	1.01	2.7	1.44
	0.147	0.77	1.38	5.7	0.90
p-Chlorophenol	0.01044	0.86	0.88	2.6	1.23
o-Cresol		.....	<0.88*	....	.....
m-Cresol	0.081	0.85	1.28	3.8	0.88
	0.162	0.79	1.04	4.1	1.10
p-Cresol	0.0699	0.80	2.23	7.9	0.53
	0.1399	0.68	2.42	17.6	0.54
Methyl alcohol**	0.005	0.97	3.54	7.9	0.284
	0.063	0.69	5.05	33.	0.26
	0.125	0.53	7.75	1300.	0.26
Benzyl alcohol**	0.019	0.92	2.32	5.6	0.45
	0.063	0.81	2.28	7.7	0.52
	0.125	0.72	2.20	12.3	0.58

*Too small to estimate.

**From data previously published in this laboratory[7].

On the basis of Hammett's[8] discussion of the effect of substituents on the benzene ring the values of K_3 are not in the right order. The results of Table II indicate that equation 1, representing models I and II, is to be favored over

On the basis of Hammett's[8] discussion of the effect of equation 2 and 3. Considering the evidence Fox and Martin[1] and of Lassettre[2] it is concluded that the dimer is represented by the linear model in which neither hydroxyl group has its normal frequency.

The effect of a second substituent next to a hydroxyl group is shown in Table III.

Table III

Compound	μ		cm.$^{-1}$		Displacement cm.$^{-1}$
	Fund.	Perturbed	Fund.	Perturbed	
o-Chlorophenol	2.776	2.825	3602	3540	62
2,4-Dichlorophenol	2.777	2.822	3610	3544	66
2,4-Dibromophenol	2.776	2.837	3602	3525	77
sym.-Tribomophenol	(2.777)	2.849	(3602)	3510	92
Pinacol	2.748	2.789	3639	3586	53
Catechol	2.777	2.809	3610	3560	50
1,1′-Dihydroxy-1,1′-dicyclohexyl	2.756	2.790	3628	3584	44

Pauling[9] traces the origin of the second band to the fact that it is possible for a hydroxyl group to exist in a cis position as well as a trans position with respect to the disturbing atom. In general, the order of the interaction of the second substituent on the hydroxyl frequency is

$$Br > Cl > OH.$$

Table IV contains a summary of the displacements of the fundamental frequencies of the hydroxyl groups in the presence of ether.

Table IV

Compound	Fund μ	Fund cm.$^{-1}$	Bonded μ	Bonded cm.$^{-1}$	Displacement cm.$^{-1}$
Pinacol	2.748 2.789	3639	2.870	3484	155
Methanol	2.74	3650	2.87	3484	166
Benzoin	(2.74)	(3650)	(2.87)	(3484)	(166)
1,1′-dihydroxyl-1,1′ dicyclohexyl	2.756 2.790	3628	2.84	3455	173
Water	2.69	3717	2.84	3521	196
Cyclohexanoneoxime	2.76	3623	2.96	3383	240
Phenol	2.77	3610	2.98	3356	254
o-Cresol	2.76	3623	2.97	3367	256

m-Cresol	2.76	3623	2.97	3367	256
p-Cresol	2.76	3623	2.97	3367	256
β-Naphthol	2.76	3623	2.98	3356	267
o-Chlorophenol	(2.77) 2.81	(3610)	3.00	3333	277
2,3-Diphenylchromenol-2	2.78	3597	3.02	3311	286
sym.-Tribromophenol	(2.77) 2.82	(3610)	3.03	3300	310
o-Nitrophenol	(2.77) 3.05	(3610)	3.05	3279	331
2,4-Dichlorophenol	(2.77) 2.81	(3610)	3.05	3279	331
p-Nitrophenol	2.78	3597	3.07	3257	340
2,4-Dibromophenol	(2.77) 2.82	(3610)	3.06	3268	342
Catechol	2.773 2.809	3606	3.066	3262	344
Pentachlorophenol	(2.77) 2.82	(3610)	3.09	3236	374
Nitromethane	2.70 2.78	3700	2.88	3470	230
Picric acid	(2.77) 3.19	(3610)	.....	.....	.....
Trichloroacetic acid	(2.84) 3.38	(3520)	.....	.....	.....
Lauric acid	(2.84) 3.36	(3520)	.....	.....	.....

The equilibrium constants for the association between the phenols and ether have been calculated from either the monomer or the association band. The results of the calculations are shown in Table V.

Table V

Compound	$\bar{K}$		$\bar{K}$
Methanol	1.7	p-Cresol	2.7
sym.-Trimromophenol	0.21	Catechol	9.1
Pentachlorophenol	0.53	Phenol	1.7
β-Naphthol	2.3	o-Chlorophenol	2.8
o-Cresol	2.2	2,4-Dichlorophenol	2.9
m-Cresol	1.9	Pinacol	3.9
		Lauric acid	5.5

In general, the shift of the hydroxyl frequency is in the order

$$\text{alcohol} < \text{water} < \text{oxime} < \text{phenols.}$$

A plot of the displacement ($cm.^{-1}$) against the logarithm of the reciprocal of the ionization constant of the corresponding compound resulted in the straight line

$$\triangle\nu = 20.3 \log K^a + 477$$

No correlation was found between the equilibrium constant and the displacement.

The normal hydroxyl group of the α,β-dihydroxyl compounds were shown to enter into hydrogen bonding with ether more readily than does the perturbed group. The dimers of the carboxylic acids are very easily broken down by ether. By means of the displacement of the hydroxyl frequency a distinction is made between two postulated forms of 2,3-diphenylchromenol-2. Evidence is presented supporting the ability of nitromethane to enolize in carbon tetrachloride solution.

In Table VI are summarized the displacements of the hydroxyl frequencies in the solid state.

Table VI

Compound	Fundamental		Band of Condensed St.		Displacement
	μ	$cm.^{-1}$	μ	$cm.^{-1}$	$cm.^{-1}$
p-Thiocresol	3.82	2620	3.86	2590	30
o-Chlorophenol (1)	2.77	3610	2.85	3509	101
β-Naphthol	2.76	3623	2.85 2.96	3510	113
sym.-Tribromophenol	2.77	3610	2.86	3497	113
Catechol	2.77	3610	2.89	3460	150
1,1′-dihydroxy-1,′1-dicyclohexyl	2.75	3623	2.96	3378	245
p-Nitrophenol	2.78	3597	3.04	3425	172
2,4-Dibromophenol (1)	2.77	3610	2.86	3497	113
2,4-Dibromophenol	2.77	3610	2.91	3436	174
2,4-Dichlorophenol	2.77	3610	2.91	3436	174
Pinacol	2.74	3650	2.90	3448	188

Pentachlorophenol	2.77	3610	2.93	3413	197
	2.82				
Quinhydrone	2.77	3610	2.96	3378	232
Terpene hydrate	2.74	3650	2.95	3389	261
m-Cresol (1)	2.76	3623	2.98	3356	267
o-Cresol (1)	2.76	3623	2.91	3436	187
o-Cresol	2.76	3623	3.00	3333	290
2-Nitroresorcinol	2.77	3610	2.79	3584	13
			3.02	3311	149
Resorcinol	2.76	3623	3.01	3322	301
o-Nitrophenol	2.78	3597	3.04	3289	308
	3.05	3278			
2,4-Dinitrophenol	2.77	3610	3.03	3300	310
Phenol	2.77	3610	3.07	3257	353
∝-Naphthol	2.76	3623	2.95	3390	233
Hydroquinone	2.76	3623	3.06	3268	355
p-Cresol (1)	2.76	3623	2.98	3356	267
p-Cresol	2.76	3623	3.09	3236	387
Cyclohexanoneoxime	2.76	3623	3.09	3236	387
			3.17	3155	468
Picric acid	2.77	3610	3.18	3145	465
2-6-Dinitrophenol	2.77	3610	3.19	3135	475
Phenanthrene picrate	2.77	3610	3.20	3125	485
sym.-Trinitroresorcinol	2.77	3610	3.21	3115	495
Suberic acid	2.84	3521	3.33	3000	518
	(3.32) **	(3010)			
Succinic acid	2.84	3521	3.35	2985	536
	(3.33) **	(3000)			
Lauric acid	2.84	3521	3.38	2959	562
	(3.36) **	(2980)			
Sebacic acid	2.84	3521	3.41	2933	588
	(3.40) **	2940			7
Glutaric acid	2.84	3521	3.34	2994	527
	(3.32) **	3010			16
Benzoic acid	2.84		3.28		
			3.28		
			3.48		
Trichloracetic acid	2.84		(3.10)		
			3.40		
			3.74		
			3.97		
			4.13		
			4.25		
			4.31		
sym.-Trinitrobenzene	3.19				

**As found in carbon tetrachloride solution.

In Table VII and VIII are tabulated the observed percentage displacements of the liquid and solid association bands from the normal fundamental monomer band.

Table VII

Compound	Liquid %	Solid %	Liquid to Solid %
p-Thiocresol	0	1.3	1.3
Phenol	6.6	10.3	3.6
o-Cresol	5.2	8.0	3.1
m-Cresol	7.3	....	....
p-Cresol	7.2	10.7	3.6
β-Naphthol	....	3.2	....
	....	6.7	....
....Resorcinol*	....	8.6	....
Hydroquinone*	....	9.8	....
Cyclohexanoneoxime	....	10.6	....
	....	12.6	....

*Davies obtained spectra difficult to interpret.

Table VIII

Compound	From the unperturbed band		From the perturbed band	
	Liq. %	Solid %	Liq. %	Solid %
2,4-Dichlorophenol	....	4.9	....	3.1
Pentachlorophenol	....	5.6	....	4.0
Catechol	....	4.2	....	3.3
2,4-Dibromophenol	3.1	4.9	1.0	2.8
sym.-Tribromophenol	....	4.9	....	0.8
o-Chlorophenol	2.8	....	1.1	....

p-Thiocresol does not show any association in the liquid state[10]. It might be strongly suspected that this is also the case in the solid state. The shift of the mercaptan frequency of p-thiocresol should then be due almost entirely to the electrostatic interactions between the molecules. The compounds capable of forming indefinite long chain polymers in the solid

state, such as phenol, p-cresol, and presumably m-cresol, have a percentage shift which greatly exceeds that of p-thiocresol.

In the case of resorcinol which does not form indefinite chains[11] one expects the liquid band to be at about 2.96 μ which would give a percentage shift of the solid band of 1.6 per cent. Carboxylic acids and the ortho nitrophenols likewise show little or no shift in the solid band. In the case of the ortho-halogenated phenols the shift of the normal monomer band lies in between that of the dimer, 2.8 per cent and of the trimer, 6.4 per cent.

In general, it can be said that those compounds which are capable of forming indefinite long chain association molecules show a considerable shift of the association band in passing from the liquid state to the solid state. Compounds which do not form these long chains, either through the formation of closed systems or through the effect of an ortho substituent, show a considerably smaller displacement.

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VITA

Ivar Trygve Krohn was born in Minneapolis, Minnesota, on January 15, 1916. He received his grammar school training in Minneapolis. He was graduated from John Marshall High School, Minneapolis, in June, 1933. During the fall of 1933 he entered the School of Chemistry of the University of Minnesota and obtained the degree, Bachelor of Chemistry, in June, 1937. He continued his studies in the graduate school of the University of Illinois from 1937 to 1941, majoring in physical chemistry. During this time he held a special research assistantship in chemistry, made possible through the Rockefeller Foundation. He is a member of Phi Lambda Upsilon, Sigma Xi, and Gamma Alpha.